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# Transesterification of canola oil over Li/Ca-La mixed oxide catalyst: Kinetics and calcination temperature investigations

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**Abstract**: In this research, a solid 1% Li/Ca-La mixed oxide catalyst was prepared using co-precipitation method followed by wet impregnation. The prepared catalyst was used in the transesterification reaction of canola oil and methanol for biodiesel synthesis. The effects of calcination and reaction temperatures were investigated on the activity of the catalyst. In addition, rate of the reaction was studied through a kinetic model for which parameters were determined. Surface properties and structure of the catalyst were characterized through the powder X-ray diffraction (XRD), thermogravimetry/derivative thermogravimetry (TG/DTG), and Fourier transform infrared spectroscopy analysis. All these emphasized that the performance of the catalyst corresponded to the generation of the active sites and their thermal activation.

**Key words**: biodiesel; heterogeneous catalyst; calcination temperature; kinetic study
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The energy crisis due to the industrialization and environmental issues caused by fossil fuels leads researchers to find green resources[1,2]. Biodiesel has become a well-known alternative in comparison to fossil fuels considering its advantages. This fuel is attractive due to being green, non-toxic, biodegradable, and renewable. Furthermore, it features low emission of hazardous materials such as CO, $NO_x$, $SO_x$, and greenhouse gasses. Biodiesel is known to be a fatty acid alkyl ester produced by the reaction of triglycerides with short-chain alcohols (e.g. methanol or ethanol). The so-called "transesterification reaction" activates over a basic or acidic catalyst or enzyme[3]. Vegetable oils, animal fats, waste oils, and algae provide the main sources of triglyceride used as feedstocks for the biodiesel production in the presence of homogeneous or solid catalysts[4]. Homogeneous basic catalysts such as NaOH and KOH are used for the production of biodiesel under mild reaction conditions on an industrial scale due to their high activity. However, such materials possess major disadvantages such as saponification problem, equipment corrosion, etc. On the other hand, researchers have focused on solid catalysts due to their recyclability and low sensitivity to moisture and free fatty acid. Moreover, there is no need for further refinement[5,6].

A number of heterogeneous catalysts have been studied for the transesterification reaction and biodiesel production[7,8]. Nevertheless, heterogeneous catalysts possess their own defects. In some cases, severe reaction conditions (i.e.; high pressure and temperature) are required to enhance the low catalytic activity[9,10]. In addition, considerable leaching of active components in the reaction mixture lead to lower activity and durability[11,12]. Calcium-based catalysts are considered to be well-known amongst solid materials for the alcoholysis of oils. However, they possess leaching problem necessitating further purifications to remove Ca components from the production media[13-15]. To enhance the performance and stability of the calcium-based catalysts, calcium was synthesized with other metal oxides as active composites[16]. D'Cruz et al[17] reported a low yield (70.7%) production of biodiesel under optimized reaction conditions for Li/CaO catalyst in the methanolysis of canola oil after 6 h of reaction. The mixed oxide of CaO-MgO showed good catalytic activity, although a significant leaching problem was reported[18]. Taufiq-Yap et al[19] reported that with $CaO\text{-}La_2O_3$ catalyst synthesized through co-precipitation, the fatty acid methyl ester (FAME) conversion of 86.51% was obtained after 6 h of reaction. In this case, the reaction time was long, and the FAME yield was lower than the standards.

In a previous work[20] of these researchers, a series of heterogeneous catalysts including different amounts of $x\text{Li/CaO-La}_2\text{O}_3$ ($x$ = 1%, 3%, 5% and 7%) were synthesized to evaluate the transesterification reaction of canola oil and methanol under different reaction conditions. After catalyst characterization, several reaction tests were performed to optimize the synthesized catalyst and the reaction conditions. Under optimum reaction conditions

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(i.e.; methanol/oil molar ratio of 15∶1, 5% catalyst and 65 ℃ reaction temperature), 1% Li/Ca-La catalyst showed the highest activity and stability amongst synthesized materials[20].

It is reiterated that, the Li/Ca-La catalyst was applied in the transesterification reaction showing promisingly superior activity and stability compared with those of the previous studies[21-23]. It was revealed that, the lithium impregnation enhanced the basic strength of the catalytic material. Moreover, the BET surface area and the durability of the catalyst were maintained even after the lithium doping took place. Thus, notable activity of the 1% Li/Ca-La catalyst was attributed to strong basic sites over the catalyst surface along with large pore sizes[20].

In the current study, focus is placed upon the impact of calcination temperature affecting the catalytic activity and surface structure of this species. Furthermore, kinetics of the reaction is modeled under optimized reaction condition.

# 1 Experimental

## 1.1 Materials

Canola oil (food-grade) was purchased from a local company (Kadbanoo Co.) and used with no further refinements. Its chemical and physical properties were listed in Table 1. Methanol and sodium hydroxide were of analytical grade (> 99%) obtained from Merck Company. Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], lanthanum nitrate hexahydrate [$La(NO_3)_3 \cdot 6H_2O$], and lithium chloride (LiCl) of analytical grades were obtained from Sigma-Aldrich Co. Distilled water was used for solution preparations.

**Table 1 Chemical and physical properties of canola oil**

| Property | Value |
|---|---|
| Oleic acid /% | 59 |
| Linoleic acid /% | 22 |
| Linolenic acid /% | 9 |
| Palmitic acid /% | 5 |
| Stearic acid /% | 3 |
| Erucic acid /% | 2 |
| Saponification value /($mg_{KOH} \cdot g^{-1}$) | 187 |
| Acid value /($mg_{KOH} \cdot g^{-1}$) | 0.071 |
| Water content /% | 0.98 |

## 1.2 Catalyst preparation

The 1% Li/CaO-$La_2O_3$ catalyst was synthesized by the following two-step method. First, CaO-$La_2O_3$ mixed oxide was prepared by co-precipitation method[24,25]. A solution of La and Ca precursors with Ca/La molar ratio of 3∶1 was obtained. Afterward, 1 mol/L solution of NaOH was added dropwise under the constant stirring rate of 80 r/min to increase the pH value up to 12. After the pH value adjustment, the solution was stirred for 5 h to ensure the complete precipitation. The precipitate was then separated and washed with deionized water for several times. This material was subsequently dried at 100 ℃ for 24 h and calcined for 3 h. In the next step, 1% of Li was impregnated upon the CaO-$La_2O_3$ mixed oxide using a rotary evaporator at 70 ℃ and 30 r/min under vacuum. Finally, the solid state was dried at 100 ℃ for 24 h and calcined for 2 h.

## 1.3 Characterizations

The powder X-ray diffraction (XRD) peaks were obtained utilizing a Rigaku RU2000 rotating anode powder diffractometer (Woodlands, TX). This was equipped with a scanning speed of 58 r/min and Cu $K\alpha$ radiation (40 kV, 40 mA), over a $2\theta$ range of 20°-100° with a step size of 0.03°.

Thermal decomposition and weight loss of the catalyst were determined through the thermogravimetric/differential thermal analysis (TG/DTG) conducted on a PerkinElmer Pyris-1 (Waltham, MA). This was performed under a flow of $N_2$ (30 mL/min) at a 15 ℃/min heating rate from room temperature to 900 ℃.

To perform Fourier transform infrared (FT-IR) spectroscopy, a KBr matrix containing catalyst samples was prepared and studied at wavenumbers ranging from 400 to 4 000 $cm^{-1}$. This analysis was performed in an ABB Bomem spectrometer where the information collected and analyzed by a data acquisition system. Spectral calculations were averaged against 32 scans with a resolution of 2 $cm^{-1}$.

The prepared FAME samples were analyzed in an Agilent Technologies, 7890A gas chromatograph equipped with a flame ionization detector (FID) and a capillary column of CP-Sill 8 CB (60 m length, 0.25 mm of diameter and 0.5 μm thickness). Furthermore, Helium was used as the carrier gas. The injector and detector temperatures were 150 and 280 ℃, respectively. Methyl ester samples were injected through a sampler at an oven temperature of 120 ℃. After an isothermal period of 4 min, the GC oven was heated-up at 7 ℃/min to 280 ℃ and maintained there for 6 min.

Hammett indicators were applied to calculate the basic strength of the catalysts at different calcination temperatures ($H_-$)[14]. Bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), indigo carmine ($H_- = 12.2$), 2, 4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$) at concentrations of

0.02 mol/L were used as indicators.

### 1.4 Experimental procedure

The reactions were carried out in a 100 mL batch reactor consisting of a three-neck flask attached to a condenser equipped with a thermometer, stirrer (fixed at a stirring power of 500 r/min) and a water bath in order to adjust the reaction temperature. All experiments were conducted at atmospheric pressure. The catalysts were activated (under atmospheric pressure and $N_2$ flow) for 30 min before the reaction started. In a typical experiment, canola oil and methanol with 5% of catalyst (in oil) and 15∶1 methanol to oil molar ratio were charged into the reactor. The reaction media was heated-up to 65 ℃ with continuous stirring at 500 r/min. Samples were withdrawn at specific time intervals (of every 30 min) by a calibrated syringe. After each experiment, the catalyst was separated from the reaction media through filtration. The rotary evaporator was used to extract excess methanol from the reaction media. The samples were then diluted with hexane and examined through GC for the FAME yield measurements.

### 1.5 FAME analysis

The FAME products were analyzed by the GC technique due to its accuracy and non-destructiveness. As the reaction product consisted of methyl esters, mono-glycerides, di-glycerides, and unreacted tri-glycerides, the ratio of biodiesel was evaluated based upon an internal standard of heptadecanoic acid as a reference material. Then the methyl ester (*i. e.*; FAME) yield was calculated through the following equation[13]:

$$\text{FAME yield (\%)} = \frac{\text{calculated weight of methyl esters}}{\text{weight of methyl ester phase}} \approx \frac{\sum f_{\text{ester}} A_{\text{ester}}}{A_{\text{reference}}} \times \frac{m_{\text{reference}}}{m_{\text{esters}}} \times 100\% \quad (1)$$

Where, $m_{\text{reference}}$, $m_{\text{esters}}$, $A_{\text{reference}}$, and $A_{\text{ester}}$ were the mass of internal standard (g), mass of methyl esters (g), area of internal standard and area of methyl ester, respectively.

## 2 Results and discussion

### 2.1 Catalyst characterization

The XRD patterns of the as-prepared samples after calcination at 100, 300, 500, 700, and 900 ℃ for 5 h are depicted in Figure 1. The Li-doped Ca-La samples showed similar characteristic peaks at 30.95°, 40.61°, 49.58°, and 56.41° due to the presence of $CaLi_2$, $Li_2O_2$, $La_2CaO$, and $Li_2O$ species, respectively, in all patterns. This indicates that the mixed metal structure of Li/Ca-La is formed. In fact, the closely similar ionic radius of La (0.106 1 nm) compared with that of Ca (0.099 nm) facilitated the substitution of La ion within the CaO lattice. Furthermore, the small radius of Li (0.076 nm) permits its incorporation into the lattice structure of Ca-La. When the calcination temperature exceeds 300 ℃, the hydroxide phases of $La(OH)_3$ (27.22°, 27.97°, 39.56°, and 48.65°) and $Ca(OH)_2$ (34.06° and 56.52°) are dehydrated leading to the formation of $La_2O_3$ (29.006° and 35.17°) and CaO (26.77° and 37.34°), respectively. In addition, there is no sign of a peak corresponding to the $LiNO_3$ species (24.71°) at the elevated calcination temperatures (>700 ℃). This suggests that $LiNO_3$ is converted into lithium oxides through thermal activation. Moreover, the XRD analysis of 1% Li/Ca-La catalyst at 700 and 900 ℃ reveals the same patterns. This indicates that the active oxide phases are completely convoluted into the material's structure.

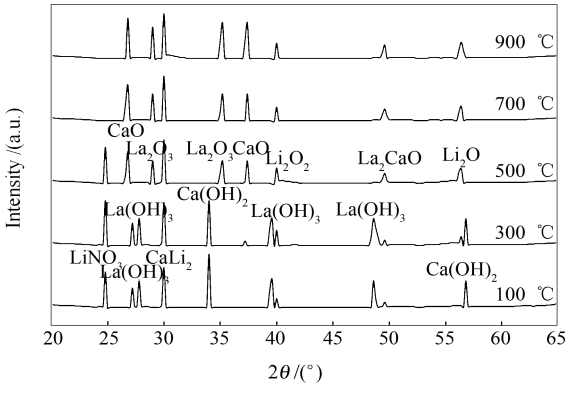


Figure 1 XRD patterns of 1% Li/Ca-La mixed oxide catalyst at different calcination temperatures

The TG/DTG curves of un-calcined 1% Li/Ca-La catalysts (after washing and drying) are demonstrated in Figure 2.

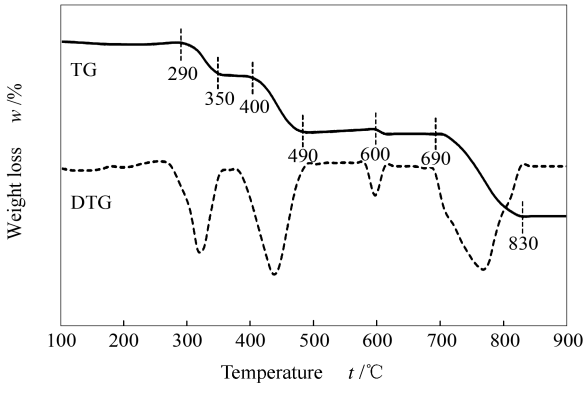


Figure 2 TG/DTG curves of 1% Li/Ca-La mixed oxide catalyst

The slight weight loss before 180 ℃ corresponds to the desorption of physically adsorbed molecules (*e. g.* $H_2O$ and $CO_2$)[26]. There are three detectable gradual weight losses for the sample. The first two main weight losses at 290 – 350 ℃ and 400 – 490 ℃ might have been due to the decomposition of $La(OH)_3$ and $Ca(OH)_2$ to $La_2O_3$ and CaO, respectively[27,28]. The transition at 600 ℃ is referred to the conversion of $LiNO_3$ to $Li_2O$, and the one at 690–830 ℃ probably appeared due to the decomposition of carbonates such as $CaCO_3$ formed with $CO_2$ of the atmosphere. The main chemical decompositions causing the weight losses are given as follows:

$$Ca(OH)_2 \xrightarrow{455\ ℃} CaO + H_2O \quad (2)$$

$$La(OH)_3 \xrightarrow{330\ ℃} LaOOH + H_2O \xrightarrow{\Delta} La_2O_3 \quad (3)$$

$$4LiNO_3 \xrightarrow{600\ ℃} 2Li_2O + 4NO_2 + O_2 \quad (4)$$

These observations are consistent with the results obtained above from the powder XRD spectra.

The FT-IR spectra for the fresh catalyst and recovered sample are shown in Figure 3.

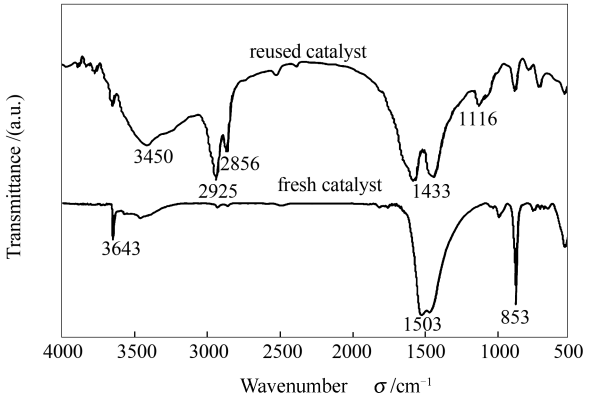


Figure 3　FT-IR spectra of fresh and used 1% Li/Ca-La mixed oxide catalyst

In the fresh sample, the sharp peak appeared at 3 643 $cm^{-1}$ is due to the free O–H bond. The bending vibration of O–Ca–O group is observed at 1 503 $cm^{-1}$ and at the low-energy region of the spectra. The weak bond at 853 $cm^{-1}$ is referable to the stretching C–O of carbonates. This suggests that the catalyst surface is altered with $CO_2$ and moisture after exposure to air. In the pattern of the recovered catalyst, there is a broad peak around 3 405 $cm^{-1}$ corresponding to the O–H bond of glycerol groups. In addition, a couple of noticeable peaks appeared at 2 925 and 2 856 $cm^{-1}$ are referable to asymmetrical and symmetric stretching of the $CH_2$ group, respectively. The FT-IR spectra of the reused material exhibit peaks at 1 433 and 1 116 $cm^{-1}$ due to the asymmetrical bending vibration of methyl group ($R-CH_3$) and the C–O group of methyl ester. This reveals that the catalyst is mainly covered with the FAME product reducing the contact surface of the methanol and catalyst. Therefore, a drop in catalytic activity is inevitable in this region[29].

The basic strengths of the prepared catalysts calcined at 100, 300, 500, 700, and 900 ℃ are determined to be 7.2–9.8, 9.8–12.2, 9.8–12.2, 12.2–15 and 12.2–15, respectively. This highlights that the Li-doped mixed oxides possess higher basic strength at elevated calcination temperatures due to generation of active sites. This is in agreement with the XRD and TG/DTG data earlier discussed above.

## 2.2　Effect of calcination temperature on catalytic activity

The leaching effect upon the calcium based catalysts might have been mitigated by performing catalyst calcination at higher temperatures to enhance the interaction of the catalyst components[30,31]. In addition, calcination temperature might have affected the basicity and BET surface area of the solid materials[32]. The effect of thermal activation on the catalyst activity was investigated for the 1% Li/Ca-La catalyst calcined at different temperatures of 100, 300, 500, 700, and 900 ℃. As depicted in Figure 4, the catalytic activity considerably depends upon the calcination temperature.

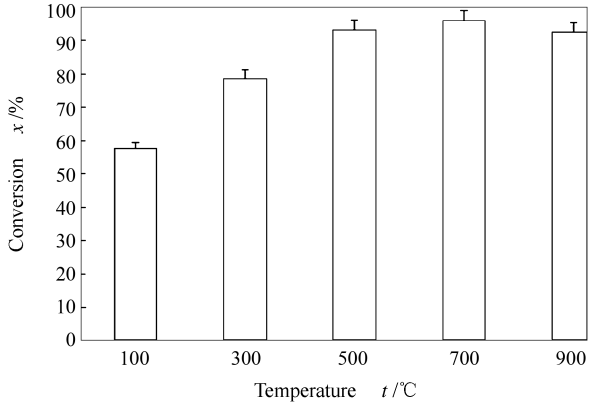


Figure 4　Effect of calcination temperature on the activity of 1% Li/Ca-La catalyst for the transesterification reaction of canola oil to FAMEs
reaction conditions: catalyst amount = 5%; methanol/oil (molar ratio) = 15∶1; temperature = 65 ℃ and reaction duration = 2.5 h

Under optimized reaction conditions of temperature of 65 ℃, methanol to oil molar ratio of 15 ∶ 1 and catalyst amount of 5%, the optimum calcination temperature is determined to be 700 ℃. The enhancement in the FAME yield of the catalyst calcined at 300 to 700 ℃ most probably is attributed

to the dehydration of the $Ca(OH)_2$ and $La(OH)_3$ phases generating the active sites. These findings are in agreement with the XRD patterns and TG/DTG analysis presented earlier in this paper.

### 2.3 Effect of the reaction temperature

A series of reactions were performed with the reaction temperature in the range of 35 to 75 ℃ in order to determine the optimum reaction temperature for the transesterification of canola oil catalyzed by 1% Li/Ca-La mixed oxide. As depicted in Figure 5.

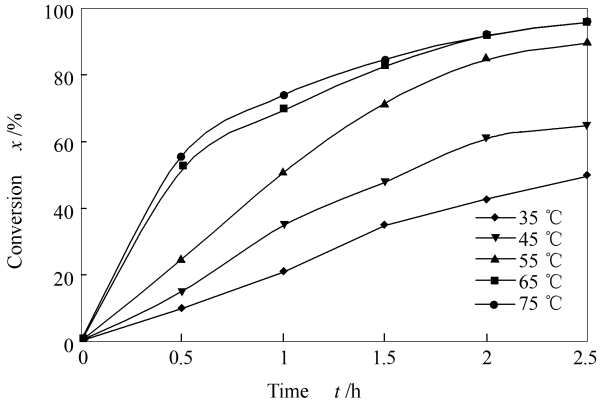


Figure 5 Effect of reaction temperature on the catalytic activity of 1% Li/Ca-La catalyst for the transesterification reaction of canola oil to FAMEs
reaction conditions: catalyst amount = 5%; methanol/oil (molar ratio) = 15∶1; calcination temperature = 700 ℃

The reaction rates are faster at higher temperatures due to lower mass resistance amongst the reaction components and higher $k$ values. The methanolysis of canola oil is enhanced with an increase in the reaction temperature up to 65 ℃ (i.e.; the reflux temperature of methanol). The mixing of canola oil and methanol at 65 ℃ shows an optimum miscibility under mild reaction conditions. Nonetheless, a further increase in the reaction temperature does not raise the rate of the reaction noticeably. Therefore, 65 ℃ is taken to be the optimized reaction temperature for the purpose at hand.

### 2.4 Kinetics of 1%Li/Ca-La catalyzed transesterification

In order to perform the kinetic study of the transesterification of canola oil catalyzed by 1% Li/Ca-La material, reaction was conducted under optimized conditions. Stoichiometric considerations lead to three moles of methanol required to react with one mole of the oil for complete conversion to biodiesel. Hence, a possibility that the reaction might have followed a 4th order chemical kinetics is raised. However, usually such reactions are performed in the presence of excess methanol thus, follow a pseudo first order kinetics[33] as follows:

$$-\ln(1-y)=kt \quad (5)$$

In which $y$ is the FAME yield at time $t$. Variations of $-\ln(1-y)$ vs $t$ for the methanolysis of canola oil at temperature range of 35–65 ℃ are shown in Figure 6.

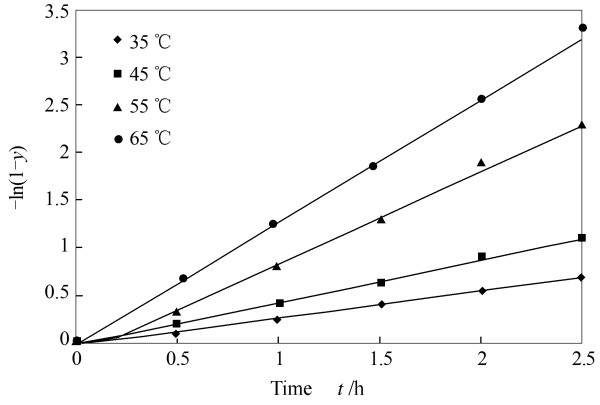


Figure 6 Graph of $-\ln(1-y)$ vs. the reaction time at different reaction temperatures
reaction conditions: catalyst amount = 5%; methanol/oil (molar ratio) = 15∶1; calcination temperature = 700 ℃

The linearity of these plots supports the idea that the reaction follows the pseudo first order kinetic model. The slopes of the respected lines provide the $k$ values at each temperature and it is found to be 1.29 $h^{-1}$ at 65 ℃. The corresponding activation energy ($E_a$) is calculated through the Arrhenius model stated in equation (6):

$$\ln k=\frac{-E_a}{RT}+\ln A \quad (6)$$

Where $R$ is the gas constant (8.314 J/(K·mol)) and $T$ is the reaction temperature (K). A graph of $\ln k$ vs $1/T$ is plotted to provide a line shown in Figure 7.

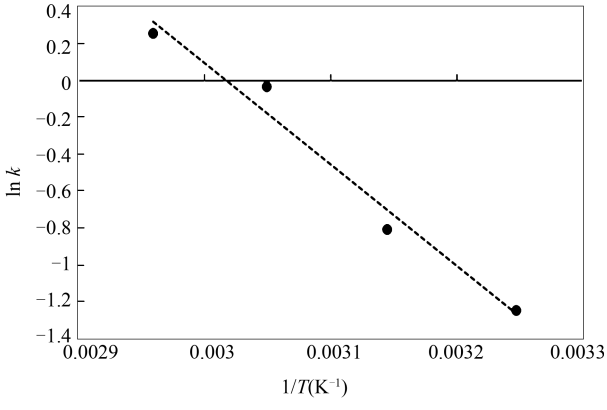


Figure 7 Arrhenius graph for the methanolysis of canola oil over 1% Li/Ca-La catalyst

The slope of the line is equaled to $-E_a/R$. The resulting $r^2$ (i.e.; the correlation coefficient) of it is

determined to be 0.975. Hence, the value of the $E_a$ is found to be 45.6 kJ/mol.

## 3 Conclusions

A 1% Li/Ca-La catalyst is found to be an active material for the transesterification reaction of canola oil with methanol. This material calcined at 700 ℃ exhibits the highest activity due to the active phases of CaO, $La_2O_3$, $Li_2O_2$ and $Li_2O$. The FAME yield of more than 96% is achieved at 65 ℃ with methanol to oil molar ratio of 15∶1 and 5% of catalyst within 2.5 h. Moreover, the reaction follows a pseudo first order kinetics under mild reaction temperatures. The values of rate constant and activation energy are determined to be 1.29 $h^{-1}$ and 45.6 kJ/mol, respectively.

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